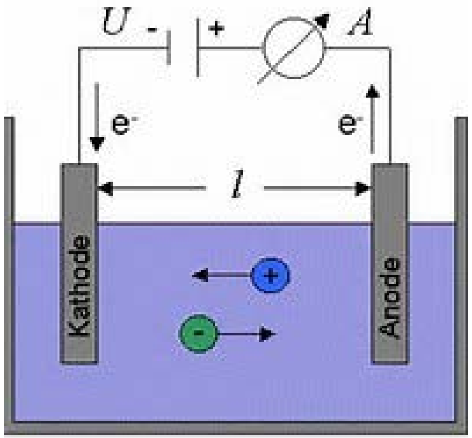
Elektrobiochemie

Stand 20.11.2020



3. Elektrobiochemie

3.1 Elektrolytische Leitung

3.1.1 Grundlagen

Kathode: $2\ H^+$ (Lösung) + $2\ e^-$(Metall) ---> $2\ H_2$ (Gas)

Anode: $2\ Cl^-$ (Lösung) ---> $2\ e^-$(Metall) + Cl_2 (Gas)

transportierte Ladung: $Q = I\ t$ (Coulomb, C, C = A s)

Faraday.Konstante: F=96 500 C mol^{-1}=$e_0\ L$=Elementarladung*Loschmidt-Zahl

Faraday-Gesetz: $Q=n\ z\ F = I\ t$

elektrisches Feld: $\mathfrak{I}=U/l$ $v_+=u_+\ \mathfrak{I}$ $v_-=u_-\ \mathfrak{I}$ u_+,u_- Ionenbeweglichkeit $(cm^2 V^{-1} s^{-1})$

Strombeitrag der Ionen: $I_+=e_0 n_+ A v_+$ $I_-=-e_0 n_- A v_-$ Gesamtstrom $I=I_+ + I_-$

$I=c\ A\ F\ (u_+ + u_-)\ \mathfrak{I}$ $I = \lambda\ A\ U / l$ mit $\lambda = c\ F\ (u_+ + u_-)$

λ Leitfähigkeit, Conductivity S/cm

Äquivalentleitfähigkeit: $\Lambda = \lambda / c = F\ (u_+ + u_-)$

3.1.2 Interionische Wechselwirkungen

Dissoziation durch thermische Molekularbewegung: $E_{th} \cong k_B T$

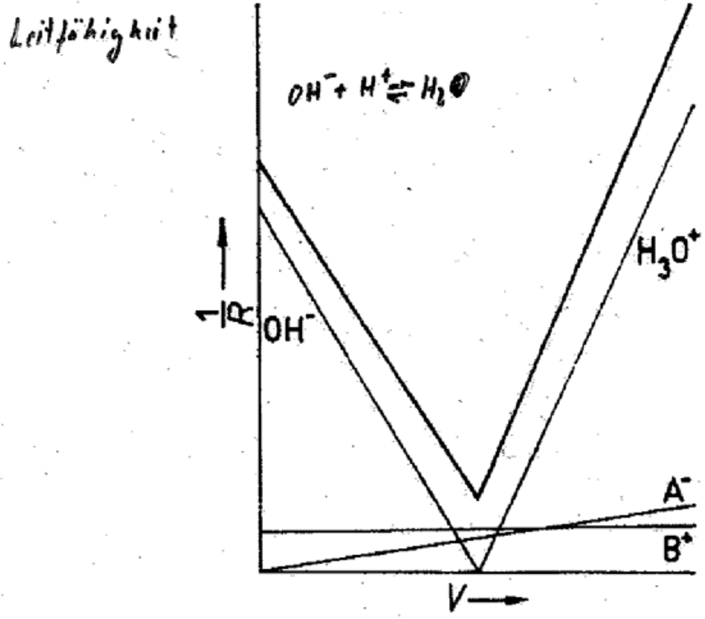
Zusammenhalt in einer „Ionenwolke“ Coulomb-Energie:

$$E_C = -\frac{q_+ q_-}{4\pi \varepsilon_0 \varepsilon r}$$

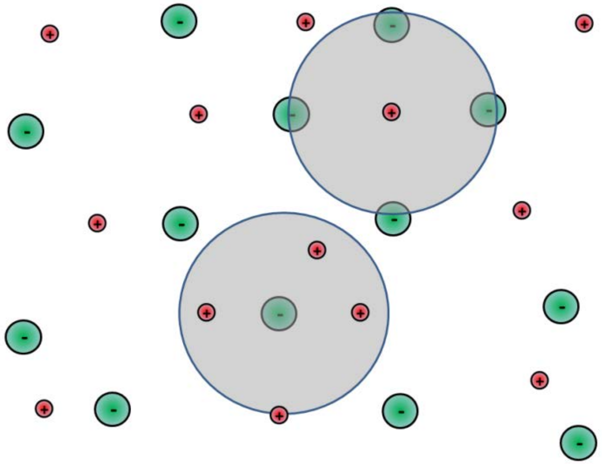
$$\boxed{\Lambda(c) = \Lambda_0 - a\sqrt{c}}$$

Kohlrausches Quadratwurzelgesetz

3.1.3 Anwendung: konduktometrische Titration



Ionenwolke



3.2 Redoxprozesse

3.2.2 Elektrochemische Zelle/ elektromotorische Kraft

Referenzelektrode: Normal-Wasserstoffelektrode ($p_H = 10^5$ Pa, $a_{H+} = 1$)

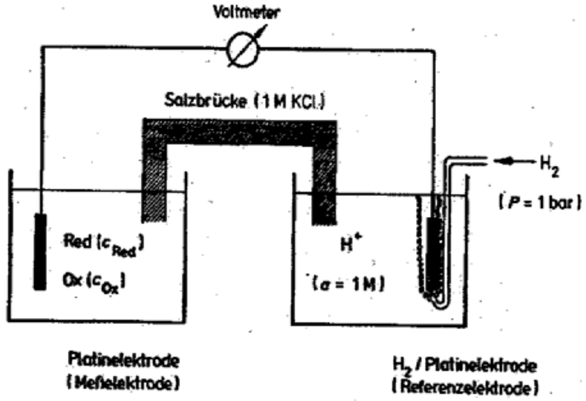
H_2 (Gas) $\Leftrightarrow$ 2 H^+ + 2 e^- (Platin)

	Meßelektrode	Referenzelektrode
a) starkes Oxidationsmittel:	Ox + e^- (Metall) ---> Red	0.5 H_2 ---> H^+ + e^- (Platin)
b) starkes Reduktionsmittel:	Red ---> Ox + e^- (Metall)	H^+ + e^- (Platin) ---> 0.5 H_2

elektrochemische Zelle: chem. Energie ---> elektrische Energie

elektromotorische Kraft: Spannung bei I -> 0; R_I (Voltm.) -> ∞; $E = \phi_{Meßelek.} - \phi_{Referenz}$

oxidierendes Red/Ox-Paar E>0, reduzierendes Red/Ox. Paar E<0

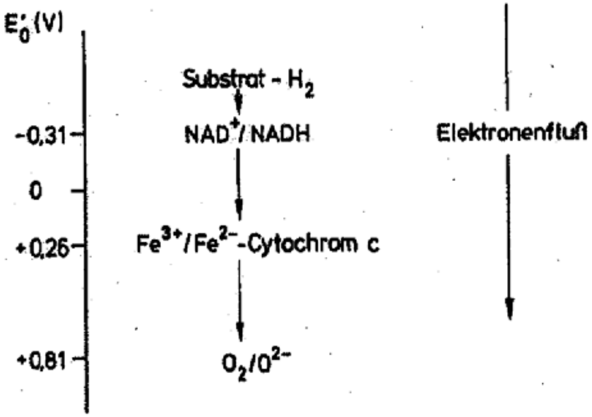


Normalwasserstoffelektrode
als Referenz unpraktisch !!!

3.2 Redoxprozesse

3.2.5 Biologische Redoxsysteme

Atmungskette, oxidative Phosphorylierung:



Photosynthetische Elektronentransportkette:

Anaerobe Atmung:

	Elektronendonor / Elektronenaceptor		Gesamtreaktion
Methanogenese	$2\ H^+/H_2$	CO_2/CH_4	$CO_2 + 4\ H_2 \dashrightarrow CH_4 + 2\ H_2O$
Acetogenese	$2\ H^+/H_2$	CO_2/CH_3COOH	$2\ CO_2 + 4\ H_2 \dashrightarrow CH_3COOH + 2\ H_2O$
Reduktion von N-Verbindungen		NO_3^-/N_2	
		NO_3^-/NO_2^-	

Chemolithotrophie (Energiegewinn aus Oxidation reduzierter anorganischer Verbindungen)

Kohlenmonoxid	CO/CO_2	O_2/O^{2-}	$CO + 1/2\ O_2 \dashrightarrow CO_2$
Wasserstoff	H_2/H^+	O_2/O^{2-}	$H_2 + 1/2\ O_2 \dashrightarrow H_2O$
Sulfid	HS^-/S	O_2/O^{2-}	$H^+ + HS^- + 1/2\ O_2 \dashrightarrow S + H_2O$
Ammoniak	NH_3/NO_2^-	O_2/O^{2-}	$NH_3 + 1{,}5\ O_2 \dashrightarrow NO_2^- + H_2O + H^+$

Redox Tower

Oxidized form	Reduced form	E'_0 (V)
[1]PS1*$_{ox}$	PS1*$_{red}$	-1.20
Ferrodoxin$_{ox}$	Ferrodoxin$_{red}$	-0.70
[2]P840*$_{ox}$	P840*$_{red}$	-0.67
Acetate	acetaldehyde	-0.60
CO_2	Glucose	-0.43
FNR$_{ox}$	FNR$_{red}$	-0.43
$2H^+$	H_2	-0.42
NADP$^+$	NADPH	-0.32
[2]PSII*$_{ox}$	PSII*$_{red}$	-0.30
Plastoquinone$_{ox}$	Plastoquinone$_{red}$	+0.14
Fumerate	Succinate	+0.03
Ubiquinone	Ubiquinone	+0.10
Cytochrome C	Cytochrome C	+0.25
Cytochrome B	Cytochrome B	+0.25
P840$^{GS}_{ox}$	P840$^{GS}_{red}$	+0.33
Cytochrome F	Cytochrome F	+0.37
PS1$^{GS}_{ox}$	PS1$^{GS}_{red}$	+0.37
Nitrate	Nitrite	+0.43
½ O	H_2O	+0.82
PSII$^{GS}_{ox}$	PSII$^{GS}_{red}$	+1.10

*Excited State, after absorbing a photon of light

^{GS} Ground State, state prior to absorbing a photon of light

[1] PS1: Oxygenic photo-system I

[2] P840: Bacterial reaction center containing bacteriochlorophyll (anoxygenic)

[3] PSII: Oxygenic phot-system II

3.2 Redoxprozesse

3.2.1 Prinzip

$$\begin{array}{ccc}
Fe^{2+} & \underset{\text{Reduktion}}{\overset{\text{Oxidation}}{\rightleftarrows}} & Fe^{3+} + e^{-} \\
Ce^{3+} & \underset{\text{Reduktion}}{\overset{\text{Oxidation}}{\rightleftarrows}} & Ce^{4+} + e^{-} \\
\hline
Fe^{2+} + Ce^{4+} & \rightarrow & Fe^{3+} + Ce^{3+}
\end{array}
\qquad
\begin{array}{ccc}
C_6H_{12}O_6 + 6H_2O & \underset{\text{Reduktion}}{\overset{\text{Oxidation}}{\rightleftarrows}} & 6CO_2 + 24H^{+} + 24e^{-} \\
6O_2 + 24H^{+} + 24e^{-} & \underset{\text{Oxidation}}{\overset{\text{Reduktion}}{\rightleftarrows}} & 12H_2O \\
\hline
C_6H_{12}O_6 + 6O_2 & \rightarrow & 6CO_2 + 6H_2O
\end{array}$$

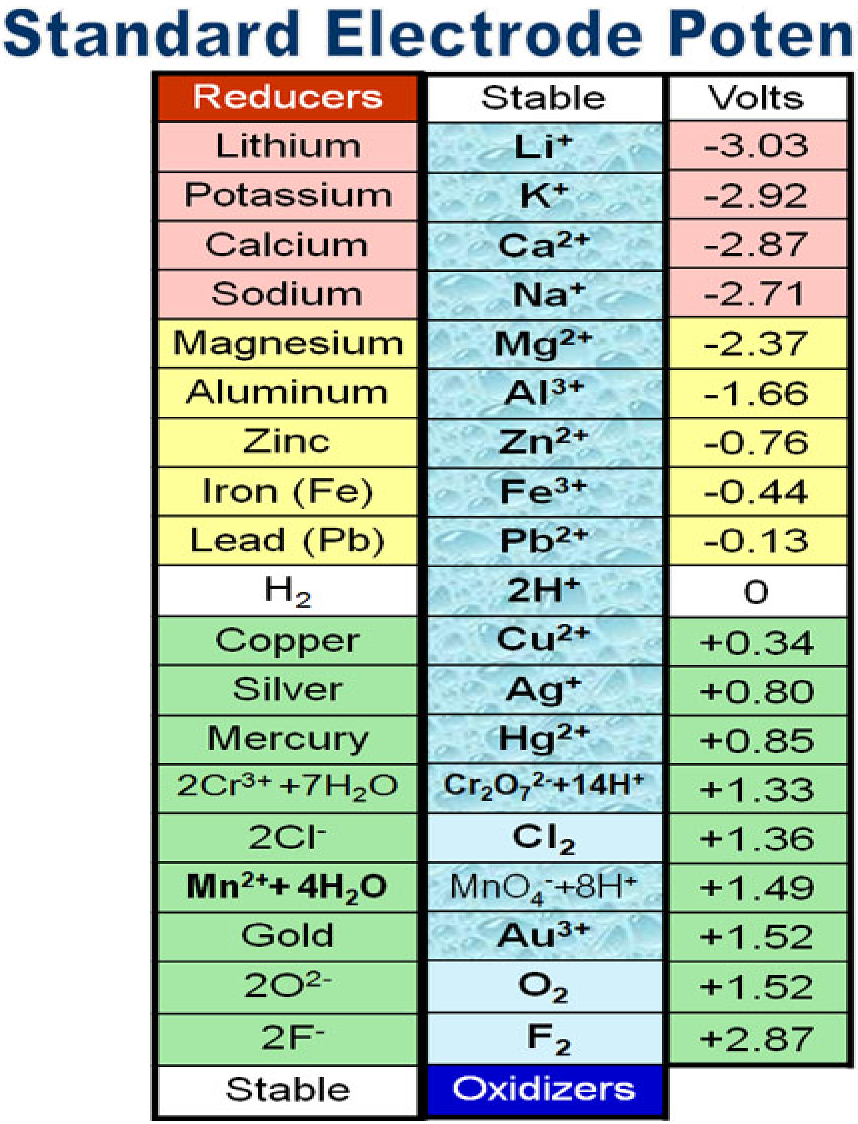
Fe^{2+}, $C_6H_{12}O_6$	- Elektronendonor, Reduktionsmittel (Red)
Ce^{4+}, O_2	- Elektronenakzeptor, Oxidationsmittel (Ox)

Allgemein:

$(Red)_1 + (Ox)_2$ ---> $(Ox)_1 + (Red)_2$

Standard Elektronenpotenziale

Leichter reduzierbar

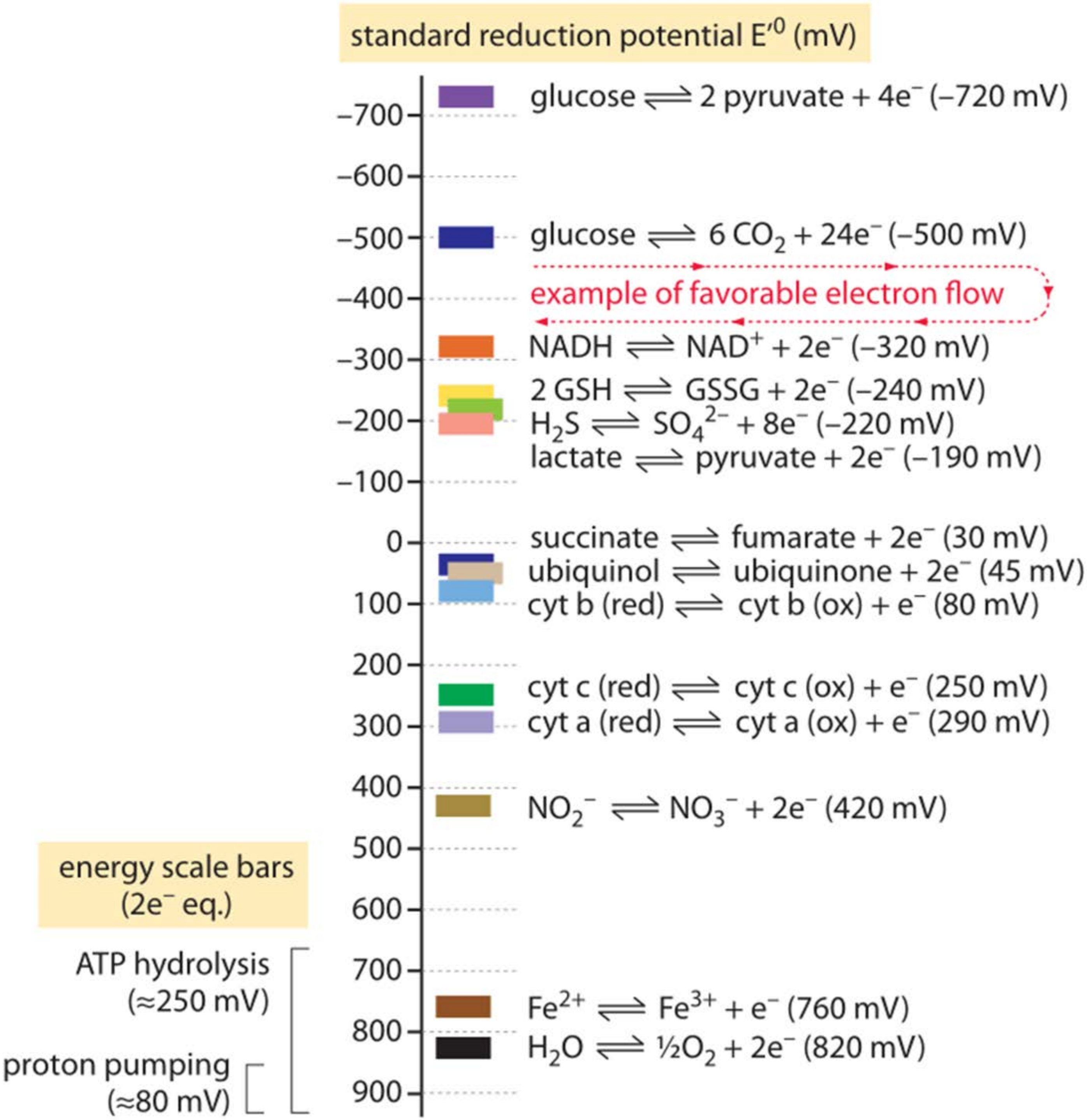


Standard Electrode Potentials

Reducers	Stable	Volts
Lithium	Li^+	-3.03
Potassium	K^+	-2.92
Calcium	Ca^{2+}	-2.87
Sodium	Na^+	-2.71
Magnesium	Mg^{2+}	-2.37
Aluminum	Al^{3+}	-1.66
Zinc	Zn^{2+}	-0.76
Iron (Fe)	Fe^{3+}	-0.44
Lead (Pb)	Pb^{2+}	-0.13
H_2	$2H^+$	0
Copper	Cu^{2+}	+0.34
Silver	Ag^+	+0.80
Mercury	Hg^{2+}	+0.85
$2Cr^{3+} + 7H_2O$	$Cr_2O_7^{2-} + 14H^+$	+1.33
$2Cl^-$	Cl_2	+1.36
$Mn^{2+} + 4H_2O$	$MnO_4^- + 8H^+$	+1.49
Gold	Au^{3+}	+1.52
$2O^{2-}$	O_2	+1.52
$2F^-$	F_2	+2.87
Stable	Oxidizers	

Leichter oxydierbar

Energie-
differenz


standard reduction potential E'^0 (mV)
–700
–600
–500
–400
–300
–200
–100
0
100
200
300
400
500
600
700
800
900
glucose $\rightleftharpoons$ 2 pyruvate + $4e^-$ (–720 mV)
glucose $\rightleftharpoons$ 6 CO_2 + $24e^-$ (–500 mV)
example of favorable electron flow
NADH $\rightleftharpoons$ NAD^+ + $2e^-$ (–320 mV)
2 GSH $\rightleftharpoons$ GSSG + $2e^-$ (–240 mV)
H_2S $\rightleftharpoons$ SO_4^{2-} + $8e^-$ (–220 mV)
lactate $\rightleftharpoons$ pyruvate + $2e^-$ (–190 mV)
succinate $\rightleftharpoons$ fumarate + $2e^-$ (30 mV)
ubiquinol $\rightleftharpoons$ ubiquinone + $2e^-$ (45 mV)
cyt b (red) $\rightleftharpoons$ cyt b (ox) + e^- (80 mV)
cyt c (red) $\rightleftharpoons$ cyt c (ox) + e^- (250 mV)
cyt a (red) $\rightleftharpoons$ cyt a (ox) + e^- (290 mV)
NO_2^- $\rightleftharpoons$ NO_3^- + $2e^-$ (420 mV)
Fe^{2+} $\rightleftharpoons$ Fe^{3+} + e^- (760 mV)
H_2O $\rightleftharpoons$ ½O_2 + $2e^-$ (820 mV)
energy scale bars
($2e^-$ eq.)
ATP hydrolysis
(≈250 mV)
proton pumping
(≈80 mV)

The energy metabolism of microorganims

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6H_2O + 6CO_2 \quad \Delta G^{\ominus\prime} = -2895 \text{ kJ mol}^{-1}$$

$$C_6H_{12}O_6 \rightarrow C_3H_7COOH + 2CO_2 + 2H_2 \quad \Delta G^{\ominus\prime} = -225 \text{ kJ mol}^{-1}$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad \Delta G^{\ominus\prime} = -206 \text{ kJ mol}^{-1}$$

$$\Delta G^{\Theta'} = n \; x \; F \; \left[E^{\Theta'}(donor) - E^{\Theta'}(acceptor)\right]$$

$$\Delta G^{\Theta'} = 24 \; x \; 96485.3 \; A\,s\,mol^{-1} \; (-0.43 - 0.82)V$$

$$\Delta G^{\Theta'} = -\,2894.55 \; kJ \; mol^{-1}$$

n = 6 * 4 + 12 * 1 + 6 * -2 = <u>24</u>

Redox couple	$E^{\ominus\prime a}$/V
CO_2/Glucose	−0.43[23]
CO_2/Formate	−0.43[23]
$2H^+/H_2$	−0.42[23]
CO_2/Acetate	−0.28[23]
CO_2/CH_4	−0.24[23]
SO_4^{2-}/HS^-	−0.22[23]
Pyrovate/lactate	−0.19[23]
Fumarate/succinate	+0.33[23]
NO_3^-/NO_2^-	+0.43[23]
MnO_2/Mn^{2+}	+0.60[24]
Fe^{3+}/Fe^{2+}	+0.77[23]
$1/2O_2/H_2O$	+0.82[23]
$1/2O_2/H_2O$	+0.51[25,26b]

[a] Standard potential, measured at pH 7. [b] Effective (irreversible) potential, determined in MFC experiments (pH 7).

$$\Delta G^{\Theta'} = 24 \; x \; 96485.3 \; A\,s\,mol^{-1} \; (-0.43 - 0.51)V$$

$$\Delta G^{\Theta'} = -\,2176.70 \; kJ \; mol^{-1}$$

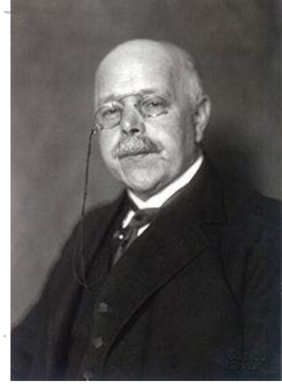
Due to:

- **Side reaction at the cathode**

  (impurities in the electrolyte and at the electrode surface)
- **Mixed potentials are formed**

3.2 Redoxprozesse

3.2.4 Nernst-Gleichung, freie Enthalpie



Walther Nernst
Habilitation in Leipzig
1864 - 1941

Nernst-Gleichung

analog zu:

$$E = E_0 + \frac{RT}{nF}\ln\left(\frac{a_{OX}}{a_{RED}}\right) = E_0 + \frac{RT}{nF}\ln\left(\frac{C_{OX}}{C_{RED}}\right) + \frac{RT}{nF}\ln\left(\frac{\gamma_{OX}}{\gamma_{RED}}\right) \qquad \Delta_R G = \Delta_R G^o + RT\ \ln\left(\frac{a_{OX}}{a_{RED}}\right)$$

Anwendung: Potentiometrie (ionenselektive Elektroden)

$$E = E_0 + \frac{25.7\,mV}{n}\ln\left(\frac{C_{OX}}{C_{RED}}\right) \quad (T = 298\,K)$$

Konzentrationsbestimmung

konstante Ionenstärke

$$\begin{array}{lcl} Fe^{2+} & \underset{\text{Reduktion}}{\overset{\text{Oxidation}}{\rightleftarrows}} & Fe^{3+} + e^- \\ Ce^{3+} & \underset{\text{Reduktion}}{\overset{\text{Oxidation}}{\rightleftarrows}} & Ce^{4+} + e^- \\ \hline Fe^{2+} + Ce^{4+} & \rightarrow & Fe^{3+} + Ce^{3+} \end{array}$$

$$\boxed{\Delta G^o = n\,F\,(E_{01} - E_{02})}$$

Extrem wichtig, weil Verknüpfung von Energie und Spannung

3.2 Redoxprozesse

3.2.5 wichtige Elektroden

Silber-Silberchlorid-Eleketrode: (E_0 = 222 mV bei 25 ° C)

$$E = E_0 + \frac{RT}{F}\ln\left(a_{Ag^+}\right) \qquad K_L = a_{Ag^+}\, a_{Cl^-}$$

$$E = E_0 + \frac{RT}{F}\ln\left(K_L\right) - \frac{RT}{F}\ln\left(a_{Cl}\right) \qquad mit\ E_0^* = E_0 + \frac{RT}{F}\ln\left(K_L\right) \qquad \boxed{E = E_0^* - \frac{RT}{F}\ln\left(a_{Cl^-}\right)}$$

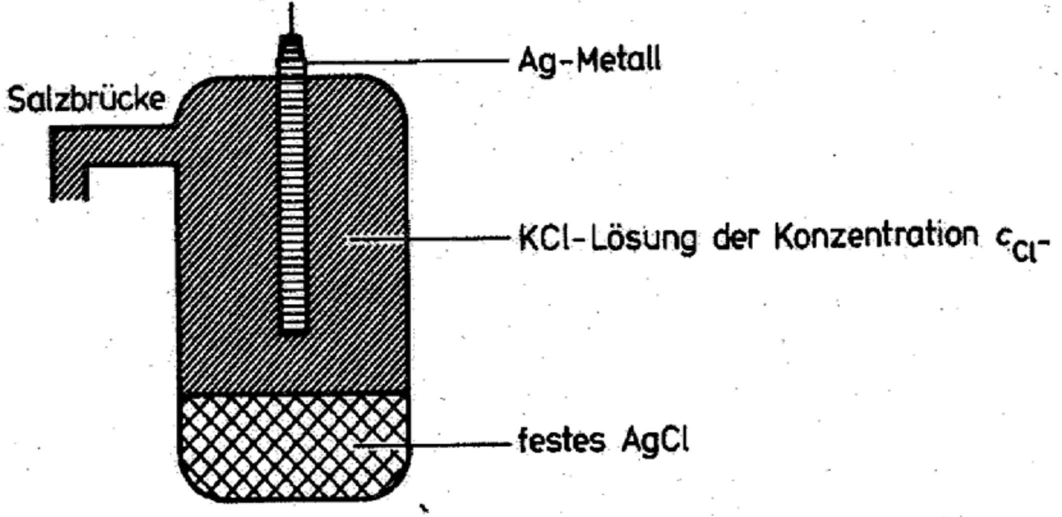


Abb. 6.12. Prinzip der Silber-Silberchlorid-Elektrode

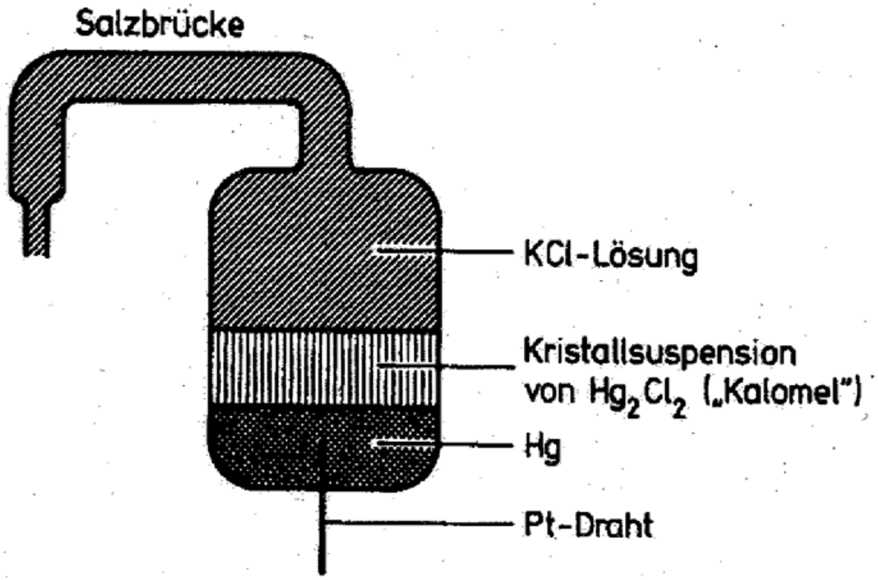
Kalomelelektrode: analog Ag/AgCl-Elektrode (268 mV) bei 25°C

Hg_2Cl_2 (Fest) $\Leftrightarrow$ Hg_2Cl_2 (gelöst) $\Leftrightarrow$ $Hg_2^{++} + 2\,Cl^-$

an der Metalloberfläche $2\,Hg \Leftrightarrow Hg_2^{++} + 2\,e^-$

$$E = E_0 + \frac{R\,T}{2\,F}\ln\left(a_{Hg_2^{2+}}\right) \qquad a_{Hg_2^{2+}} = \frac{{a_{Cl^-}}^2}{K_L}$$

$$\boxed{E = E_0^* - \frac{R\,T}{F}\ln\left(a_{Cl^-}\right)} \qquad mit\ E_0^* = E_0 + \frac{R\,T}{2\,F}\ln\left(K_L\right)$$

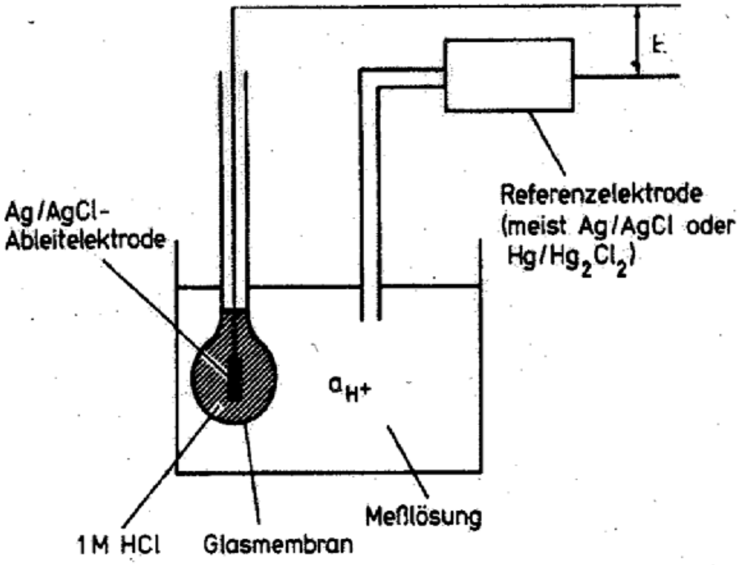


Glaselektrode:

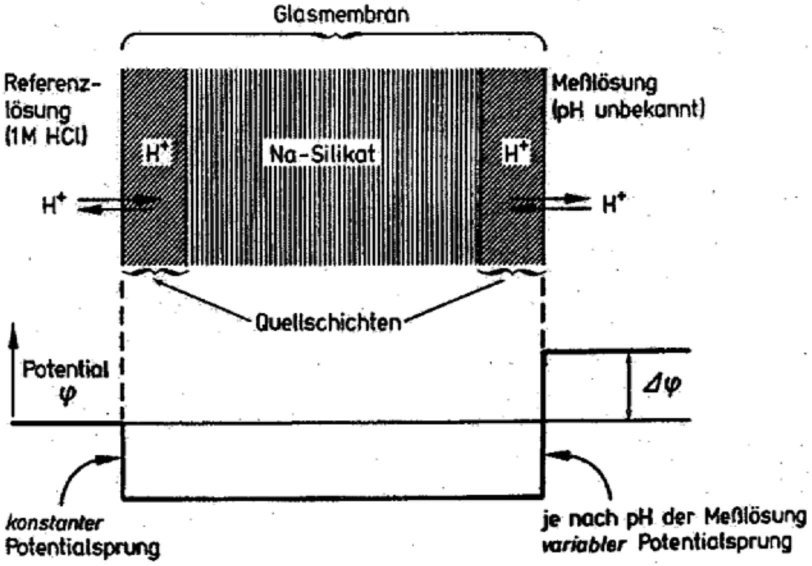
$$E = E_{0}^{*} + \frac{RT}{F}\ln\left(a_{H^+}\right)$$

$$aus \quad pH = -\lg\left(a_{H^+}\right) \; folgt:$$

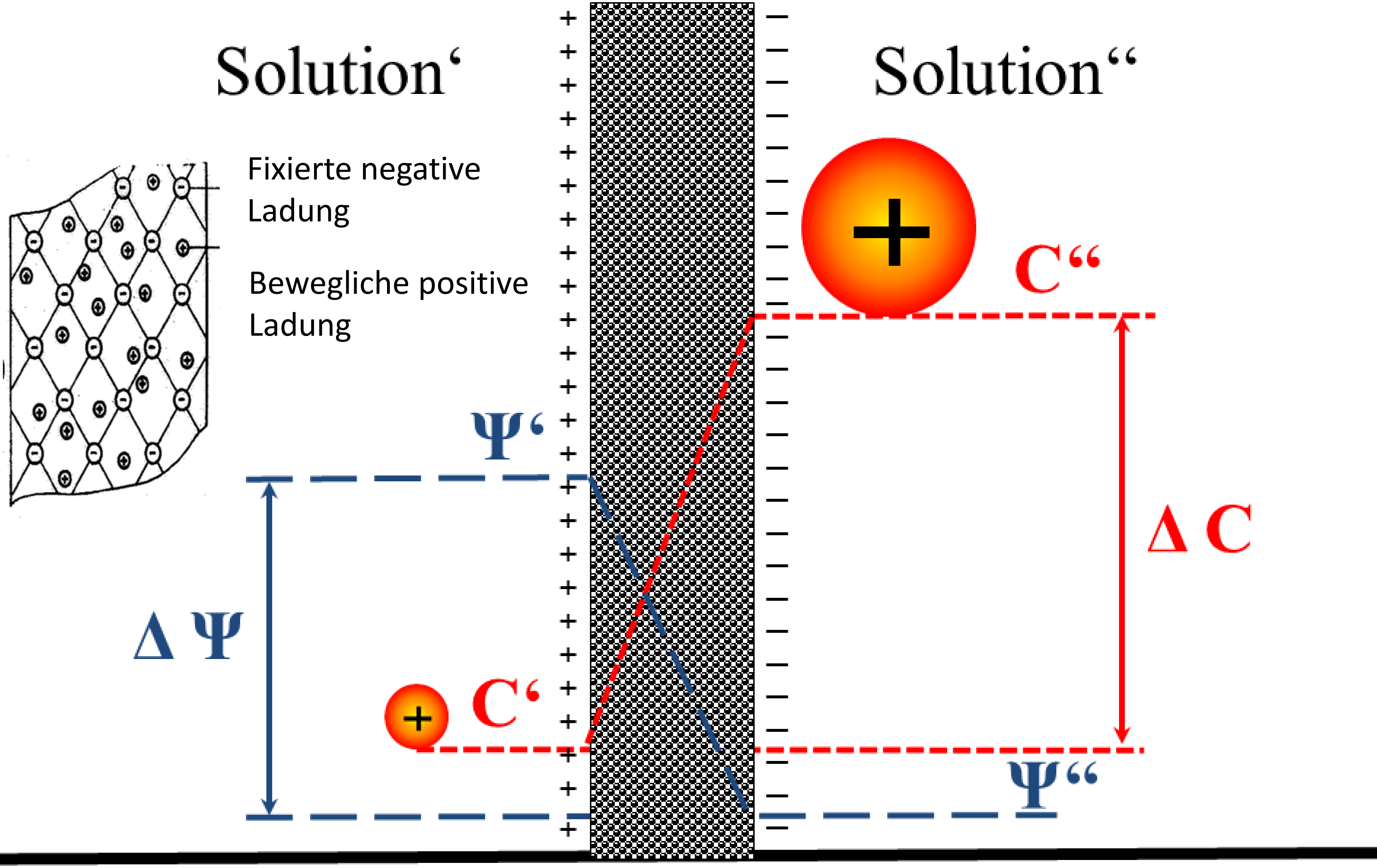
$$E = E_{0}^{*} - (59.2\,mV)\,pH$$



Zweipunkt-Kalibration mit Puffern (Üblich pH=4.00 und pH=9.00)



Ionengleichgewichte an Membranen/ionenselektive Elektroden



Solution‘

Solution“

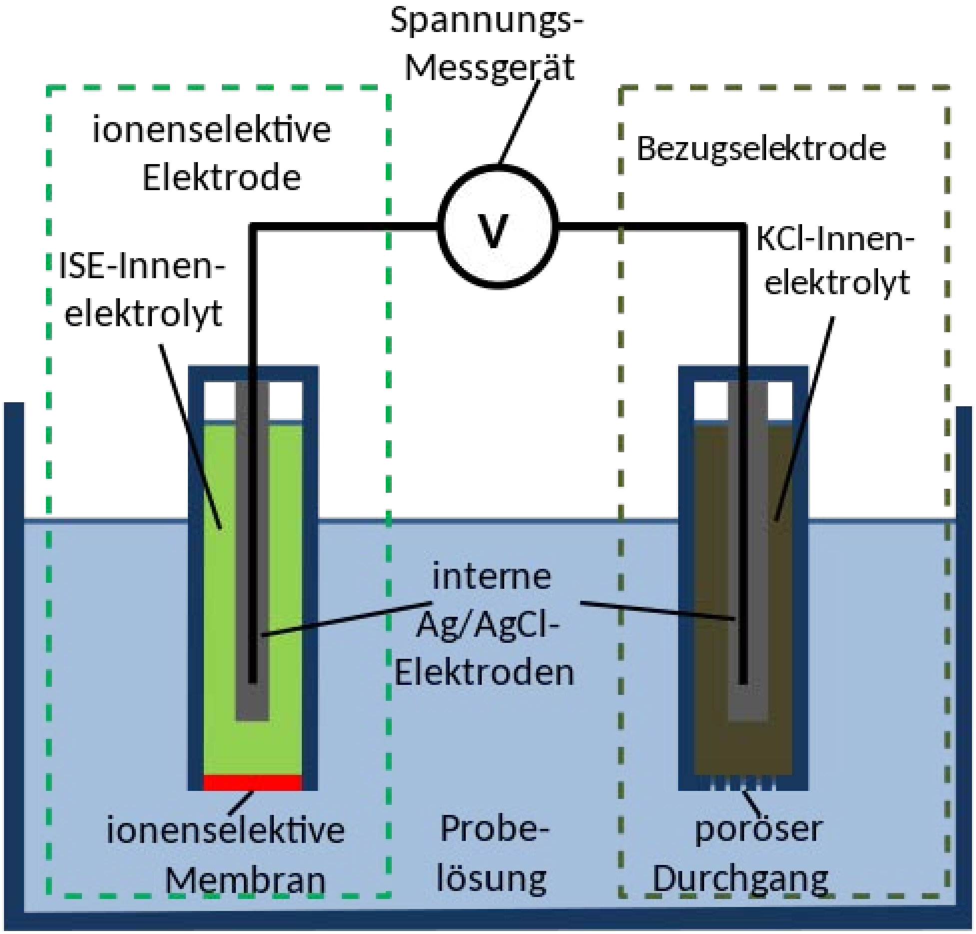
Fixierte negative Ladung

Bewegliche positive Ladung

Anwendung als Ionenselektive Elektrode

Anwendbar für Kationen:

H^+
Na^+
K^+
Ag^+
NH_4^+
Cu^{2+}
Pb^{2+}
Ca^{2+}
Cd^{2+}
Ba^{2+}



Anwendbar für Anionen:

F^-
Cl^-
Br^-
I^-
HS^-
NO_3^-
CN^-
SCN^-

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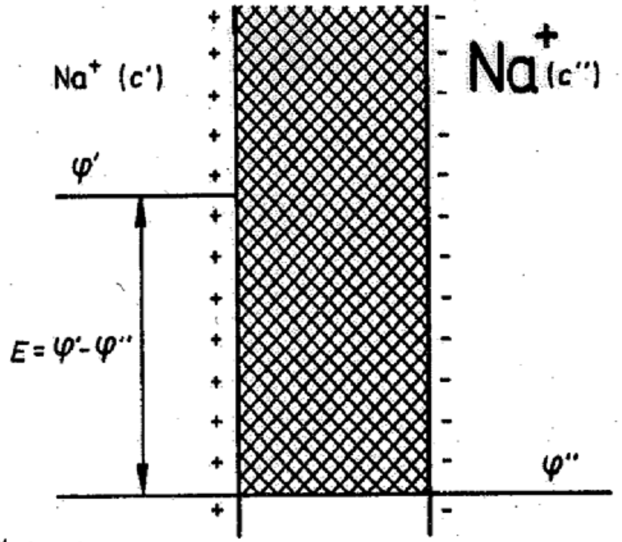
3.4 Ionengleichgewichte an Membranen



Neu: das elektrochemische Potenzial

Elektrochemisches Potential und Gleichgewichtsbedingung

$$\tilde{\mu}_i = \mu_i + z_i\, F\, \varphi = \mu_i^0 + RT\ln(a_i) + z_i\, F\, \varphi \qquad aus\ \mu_i^{\,I} = \mu_i^{\,II}\ wird\ \tilde{\mu}_i^{\,I} = \tilde{\mu}_i^{\,II}$$

$$\mu_+^{\,I} + z_i\, F\, \varphi^I = \mu_+^{\,II} + z_i\, F\, \varphi^{II}$$

$$\mu_+^0 + RT\ln\left(a_+^I\right) + z_i\, F\, \varphi^I = \mu_+^0 + RT\ln\left(a_+^{II}\right) + z_i\, F\, \varphi^{II} \qquad E = \varphi^I - \varphi^{II}$$

$$\boxed{E = \varphi^I - \varphi^{II} = \frac{RT}{zF}\ln\left(\frac{a_+^{II}}{a_+^I}\right)}$$

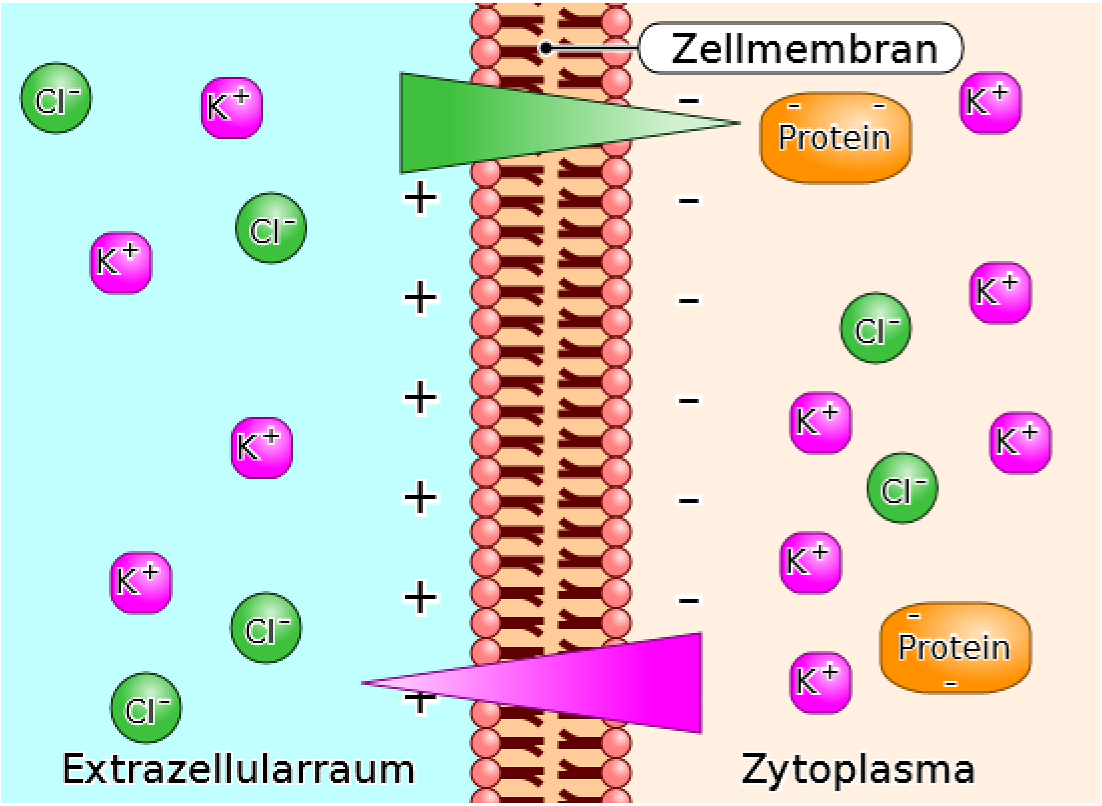
Nernst-Gleichung, Membranpotential,

Nernst-Potential

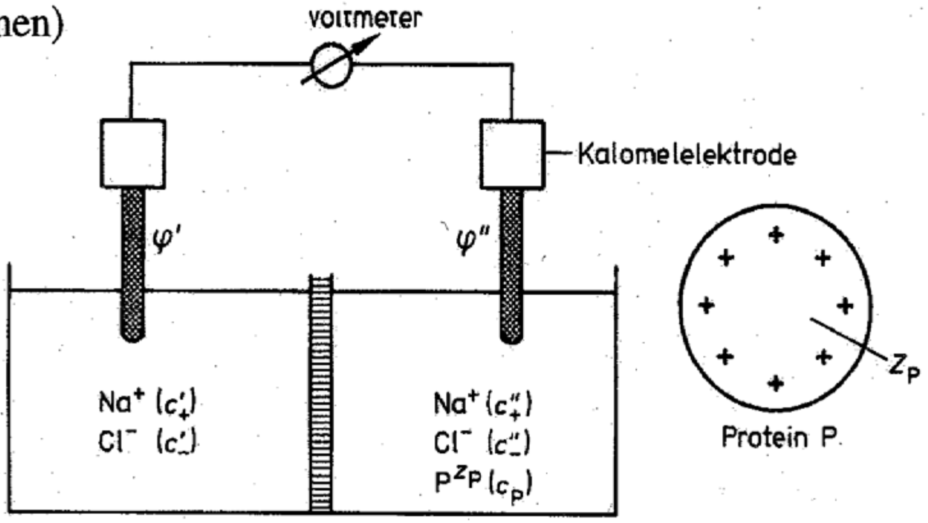
Anwendungsbeispiele – elektrochemisches Potenzial

"That's all well and good, but what's the practical application for it?"

Anwendungen Donnan Gleichgewicht



Donnan-Potential: (Polyelektrolyte, z.B. Proteine basisch: -NH_3^+ oder sauer -COO^-; Ladungszustand von Proteinen)



Membran, für Na^+ und Cl^- permeabel, für Protein P impermeabel

Grundidee: Ein Polyelektrolyt bindet Gegenionen, verändert das elektrochemische Potential

$$\tilde{\mu}_+^I = \tilde{\mu}_+^{II} \qquad \mu_+^0 + RT\ln\left(a_+^I\right) + F\varphi^I = \mu_+^0 + RT\ln\left(a_+^{II}\right) + F\varphi^{II}$$

$$\tilde{\mu}_-^I = \tilde{\mu}_-^{II} \qquad \mu_-^0 + RT\ln\left(a_-^I\right) - F\varphi^I = \mu_-^0 + RT\ln\left(a_-^{II}\right) - F\varphi^{II}$$

Addition führt zu: $\boxed{c_+^I\, c_-^I = c_+^{II}\, c_-^{II}}$ Donnan-Gleichung

Donnan-Potential: Anwendung

Seite ohne Protein (I):

Seite mit Protein (II):

$$c_-^{II} = z_p\, c_p + c_+^{II} \qquad \left(C^I\right)^2 = C_+^{II} \cdot \left(C_+^{II} + z_P \cdot C_p\right)$$

$$c_+^I = c_-^I = \left(c^I\right)^2 = c_+^{II}\, c_-^{II}$$

$$0 = \left(C_+^{II}\right)^2 + C_+^{II} \cdot z_P \cdot C_p - \left(C^I\right)^2$$

Konzentration der Kationen auf der Proteinseite (II): $c_+^{II} = \sqrt{\left(c^I\right)^2 + \left(\frac{z_p\, c_p}{2}\right)^2} - \frac{z_p\, c_p}{2}$

Konzentration der Anionen auf der Proteinseite (II): $c_-^{II} = \sqrt{\left(c^I\right)^2 + \left(\frac{z_p\, c_p}{2}\right)^2} + \frac{z_p\, c_p}{2}$

Salzkonzentration groß $c^I \gg |\, z_P c_P \,|$

$$c_+^{II} \approx c^I - \frac{z_P\, c_p}{2}$$

$$c_-^{II} \approx c^I + \frac{z_P\, c_p}{2}$$

Salzkonzentration klein $c^I \ll |\, z_P c_P \,|$

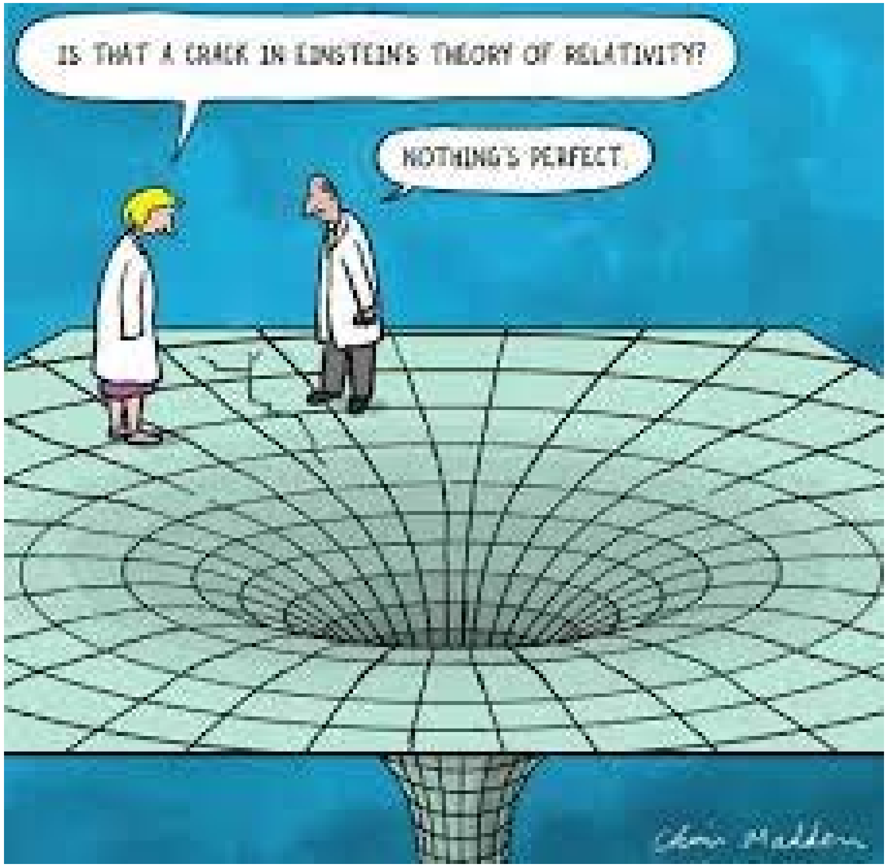
$$c_+^{II} \approx 0$$

$$c_-^{II} = z_p\, c_p$$

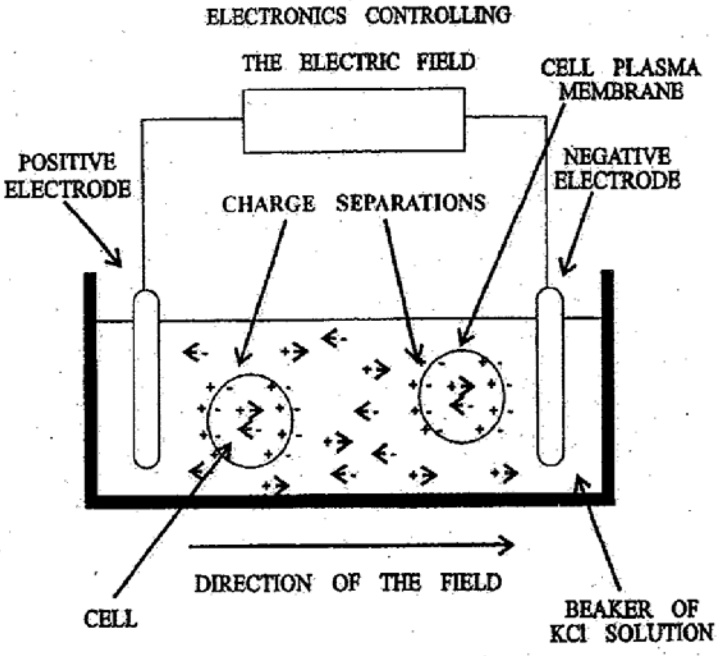
$$E = \varphi^I - \varphi^{II} = \frac{RT}{F} \ln\left(\frac{c_+^{II}}{c_+^I}\right) = -\frac{RT}{F} \ln\left(\frac{c_-^{II}}{c_-^I}\right)$$

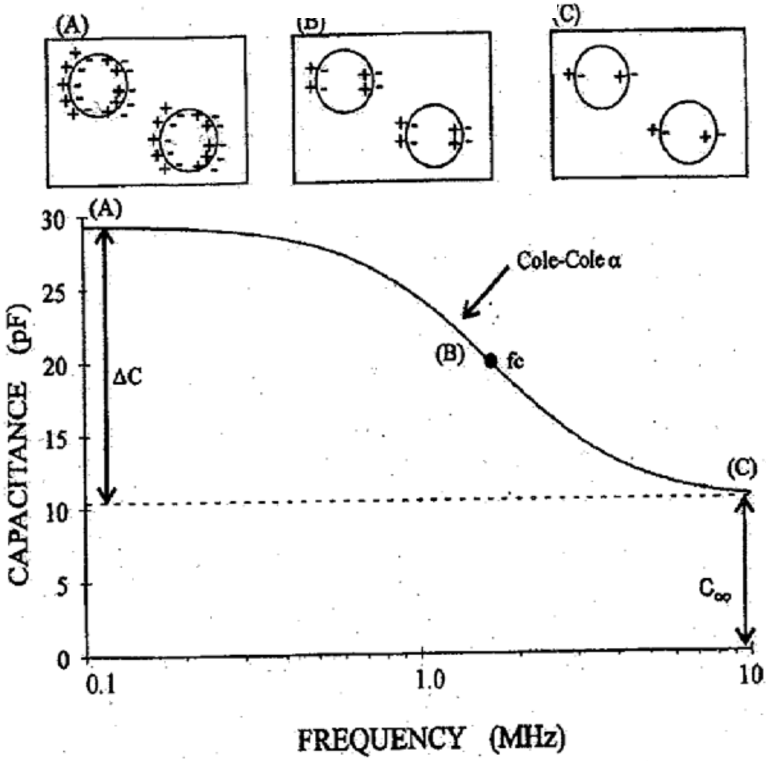
Spannung -> Ladungszustand des Proteins

Andere wichtige Anwendungen der Elektrobiochemie



Dielektrische Spektroskopie

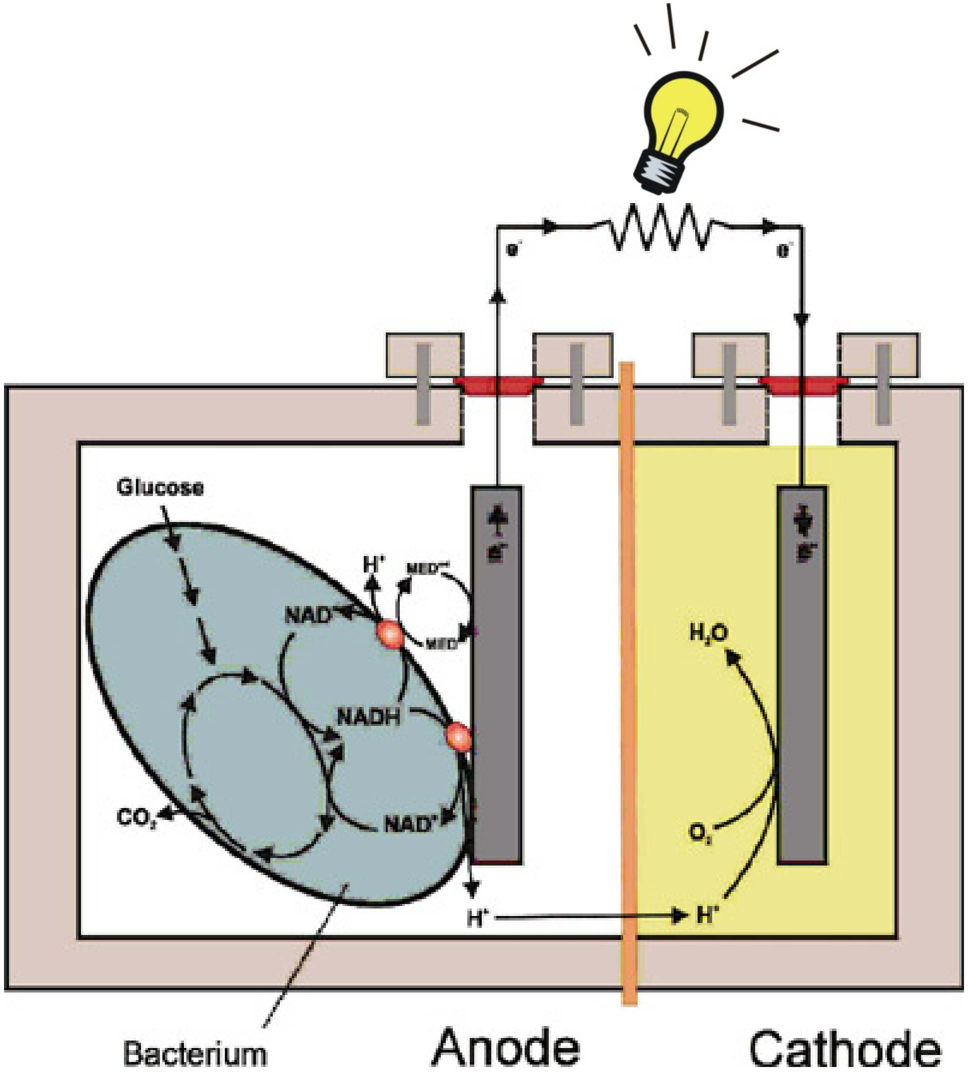




ΔC ~ intaktem Biovolumen

f_c - Info über mittlere Zellgröße

Mikrobielle Brennstoffzelle



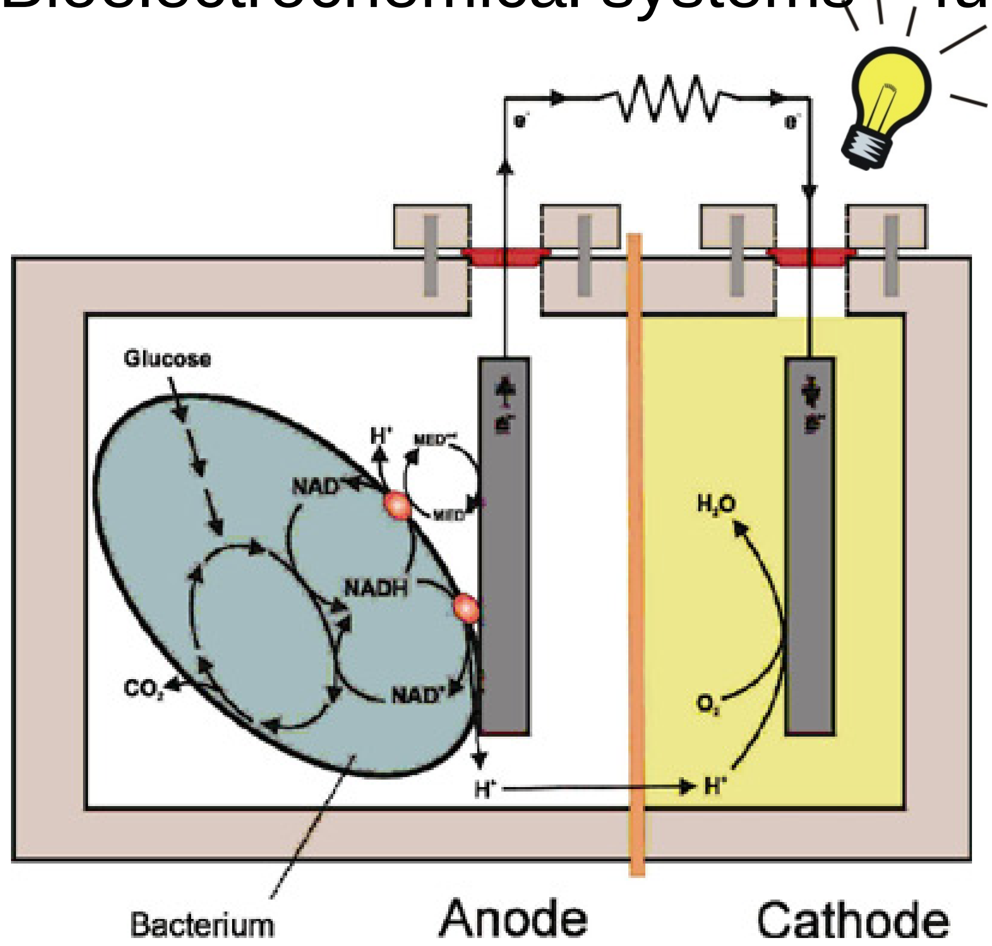
$C_6H_{12}O_6 + 6\ H_20 ->$

$6\ CO_2 + 24\ H^+ + 24\ e^-$

$O_2 + 4\ H^+ + 4\ e^- ->$

$2\ H_2O$

BES – Bioelectrochemical systems – für Synthesen ?



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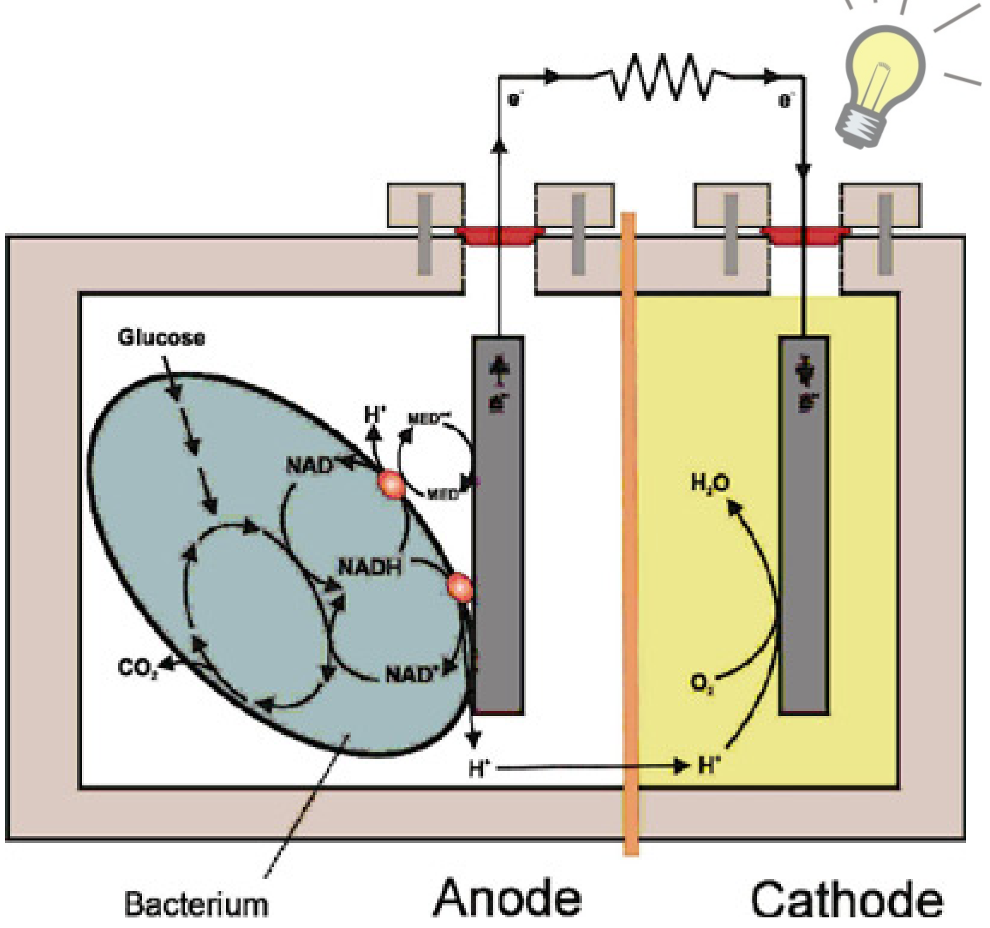

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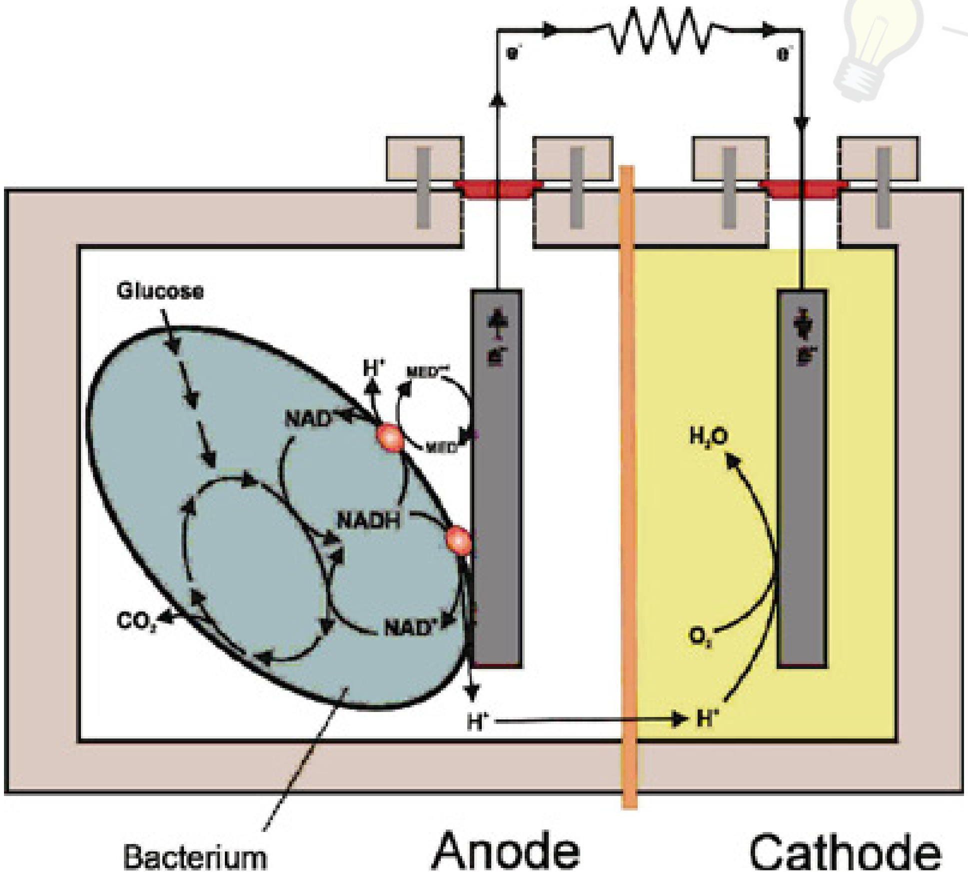

$C_6H_{12}O_6 + 6\ H_20 \rightarrow$

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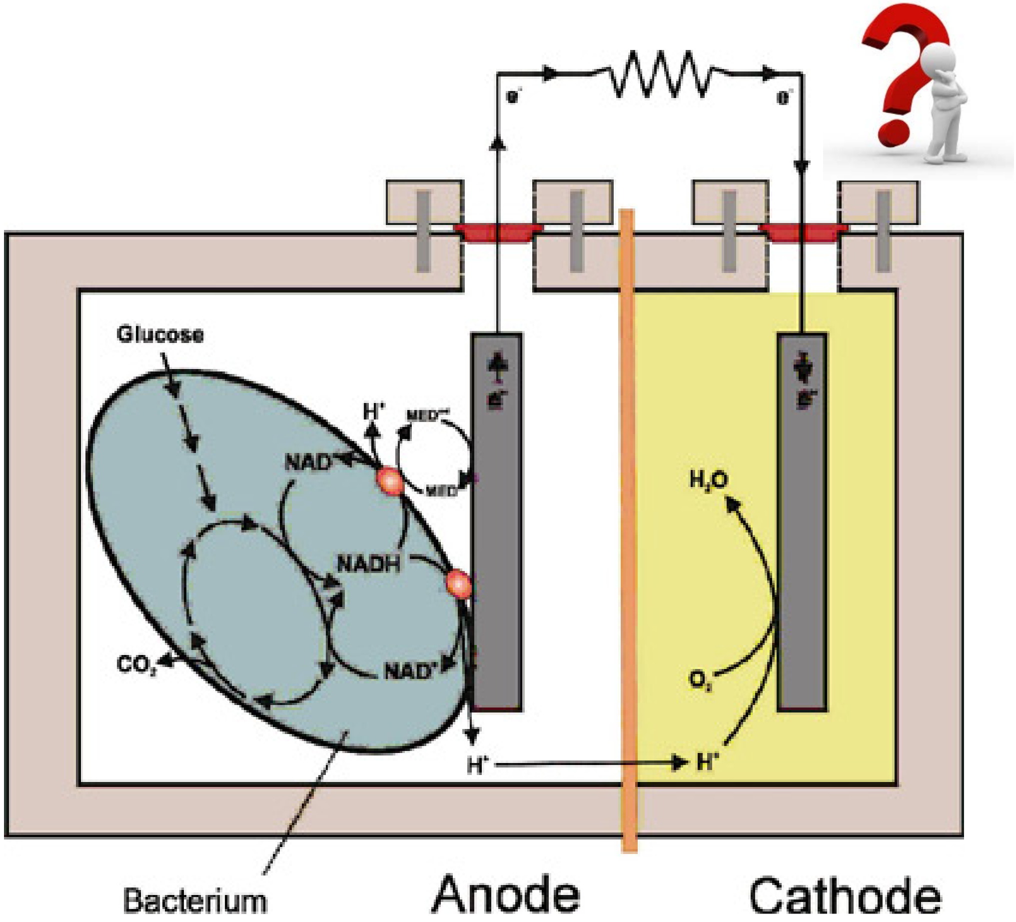
$CO_2 + 8\ H^+ + 8\ e^- \rightarrow 2\ H_2O + CH_4$ (98 mV)

BES – Bioelectrochemical systems – für Synthesen ?



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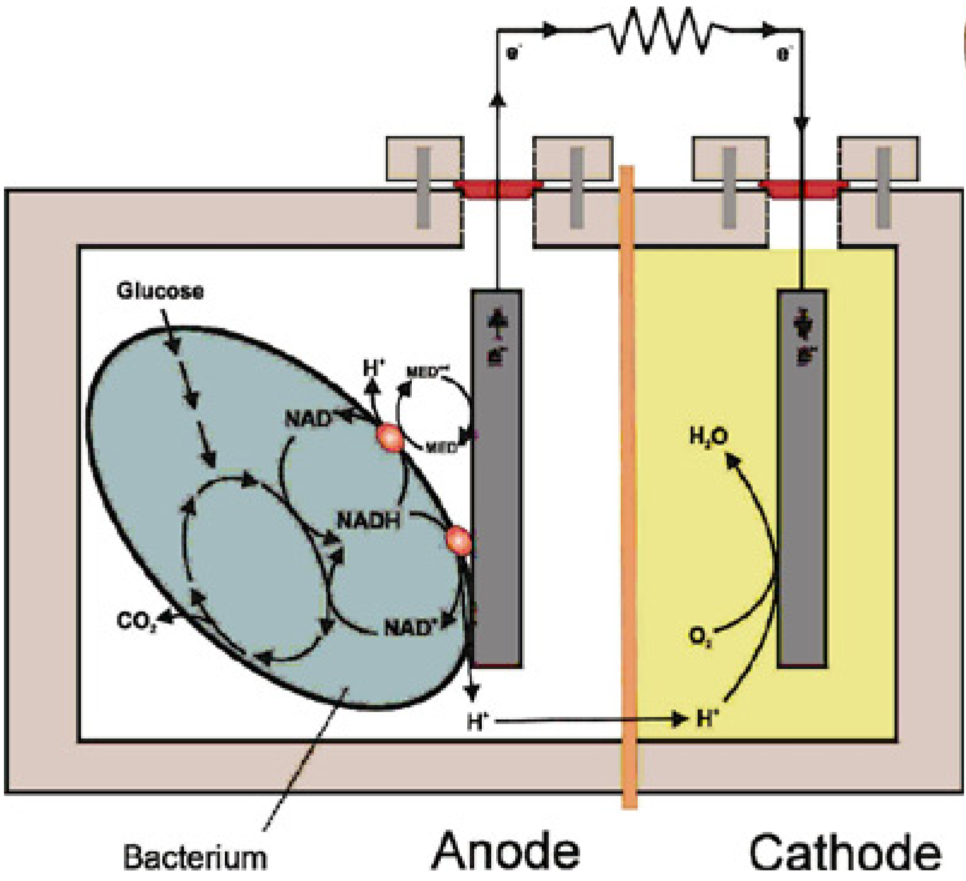
2 H^+ + 2 e^- -> H_2 (- 76 mV)

BES – Bioelectrochemical systems – für Synthesen ?



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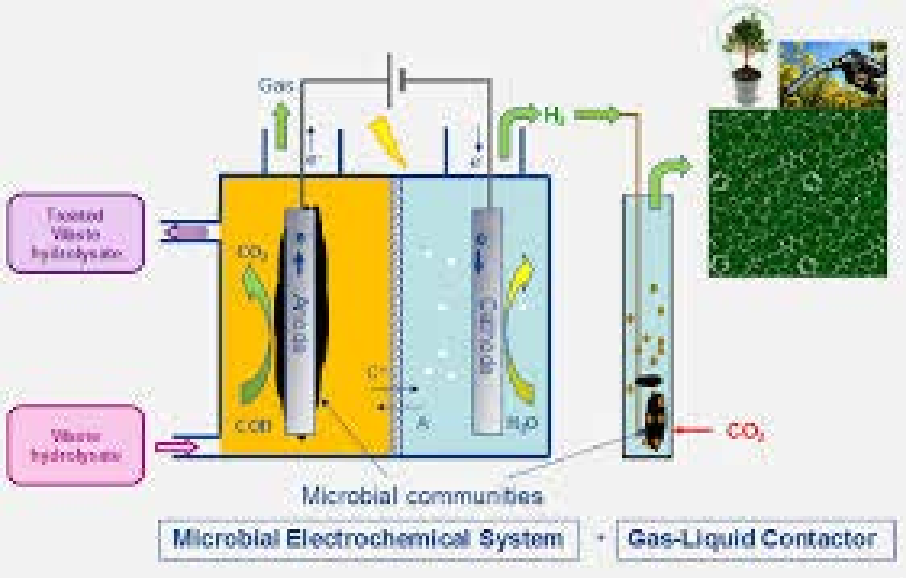
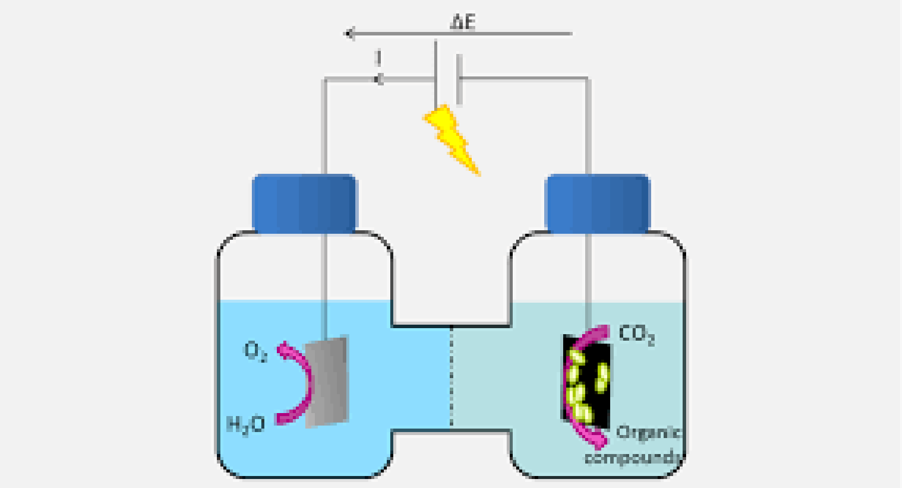
2 H^+ + 2 e^- -> H_2 (- 76 mV)

For instance ... to fix CO_2



indirekt

Microbial electrosynthesis system (MES) used for organic compounds production through carbon dioxide reduction, comprising a biotic cathode (right) coupled to abiotic anode (left)



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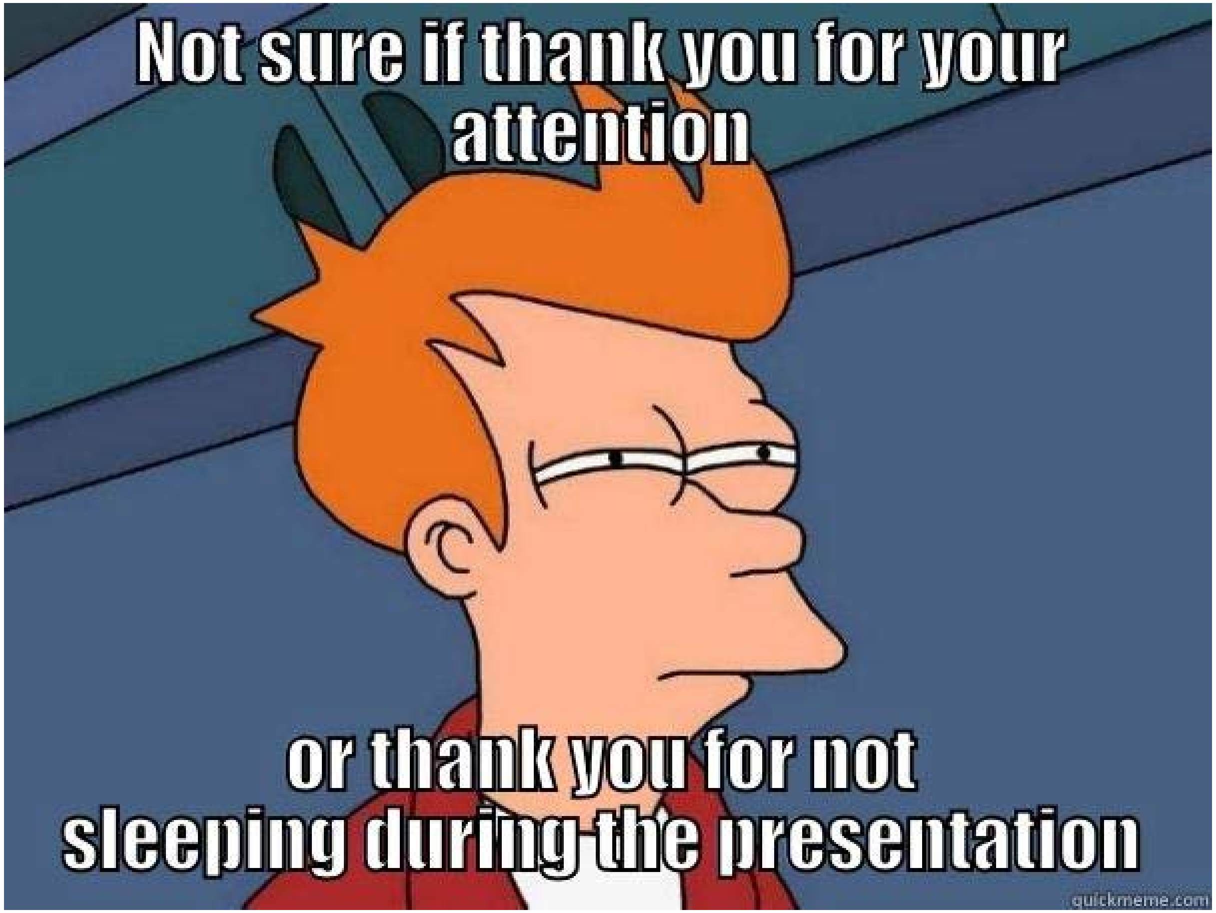
Danke für die Aufmerksamkeit



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